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The Effect of the Addition of Sulfonate-Doped-Polypyrroles on the Dielectric Properties of Polypyrrole/Silicone Composites

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Defence R&D Canada – Atlantic

Technical Memorandum

DRDC Atlantic TM 2003-249

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Canada

105-04548/

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Abstract

Dielectric polymer actuators that utilize the Maxwell stress effect consist of a thin membrane of elastomer sandwiched between compliant electrodes. When an electrostatic charge is applied across the electrodes, the oppositely charged electrodes attract, resulting in an expansion of the polymer in the plane normal to the compression. In order to maximize performance, the dielectric layer must be non-conducting and have a low Young's modulus and a high dielectric constant. Increasing the dielectric constant of an elastomer can be achieved by adding conductive fillers below the percolation threshold. The goal of this research was to increase the dielectric constant of a silicone elastomer through the addition of a conducting polymer filler. Three different sulfate doped polypyrroles (PPy) were synthesized using a literature method. Composite films using the PPy+dopant filler and a high strength silicone were formed and used to study the effects of changing the dopant and the PPy:silicone ratio on the dielectric properties of the composite film. The different dopant counterions used were sulfate (SO_4^{2-}), ethylbenzene sulfonic acid (EBSA) and polystyrene sulfonate (PSS). The conductivity of the PPy+dopant was found to increase as PPy–SO_4^{2-} < PPy–EBSA < PPy–PSS. Increasing the weight percent of PPy+dopant in the silicone matrix corresponded to an increase in the permittivity. These results supply valuable information for the use of high dielectric polymers in actuator and energy storage applications.

Résumé

Les actionneurs à base de polymère qui utilisent l'effet de stress Maxwell consistent d'une mince membrane d'élastomère entre deux électrodes conformes. Lorsqu'une charge électrostatique est appliquée entre les électrodes, les électrodes de charge opposée s'attirent, ce qui résulte en une expansion du polymère dans le plan normal à la force de compression. Pour maximiser la performance, le polymère doit être isolant, avoir un bas Module de Young et avoir une grande constante diélectrique. Il est possible d'augmenter la constante diélectrique d'un polymère en y ajoutant une charge conductrice sous le seuil de percolation. Le but de cette recherche était d'augmenter la constante diélectrique d'un élastomère à base de silicone en y ajoutant une charge conductrice. Utilisant une méthode tirée de la littérature, trois différents polypyrroles (PPy) dopés au sulfate ont été synthétisé. Des films composites utilisant la charge de PPy+dopant et un silicone à haute résistance ont été créés et utilisés pour déterminer l'effet de la variation du dopant et de la fraction PPy :silicone sur les propriétés diélectrique des films composites. Les trois différent contre-ions dopants utilisés était le sulfate (SO_4^{2-}), l'acide sulfonique

éthylbenzène (EBSA) et le sulfonate de polystyrène (PSS). La conductivité des PPy+dopant augmente tel PPy–SO_4^{2-} < PPy–EBSA < PPy–PSS. L'augmentation du pourcentage massique de PPy+dopant dans la matrice de silicone résulte en une augmentation de la permittivité. Ces résultats fournissent de l'information indispensable pour l'utilisation des polymères à haute constante diélectrique dans le domaine des actionneurs et dans le domaine d'entreposage d'énergie.

Executive summary

Background

Actuating materials can be found in a large number of applications. Common examples include piezoelectric, electrostrictive, magnetostrictive and shape memory materials. The recent advances in smart materials have led to a new class of actuators utilizing dielectric elastomeric polymers. These actuators have shown a lot of potential and are envisioned for use in active vibration isolation for military platforms. Dielectric polymer actuators utilize the Maxwell stress effect. In order to do so, the elastomeric membrane must be non-conducting and have a low modulus and a high dielectric constant. Increasing the dielectric constant of an elastomer can be achieved by varying its chemical composition or adding fillers such as conductive particles. It has been shown that the dielectric constant can be increased by factors as large as 10^4 for composites containing as little as 3% v/v carbon black [1]. Our goal is to mimic such large increases using a conducting polymer as the filler. The research discussed here will deal with synthesis of the conducting polymer polypyrrole, and the formation of elastomeric composite films using doped polypyrrole and high strength silicone. The effects of changing the dopant ions in the polypyrrole and varying the polypyrrole:silicone ratio on the dielectric properties of the composite elastomers are discussed.

Principal Results

The research reported here has two main thrusts. First, polypyrrole (PPy) was synthesized using established literature methods. Three batches were made, each incorporating a different dopant to oxidize the PPy. The three dopants were ethylbenzene sulfonic acid (EBSA), polystyrene sulfonate (PSS), and sulfate ion (SO_4^{2-}). The resulting PPy–EBSA, PPy–PSS and PPy–SO_4^{2-} were analyzed to verify polymerization and determine degree of PPy oxidation. It was found that the degree of oxidation was PPy–SO_4^{2-} <PPy–EBSA <PPy–PSS.

The second part of this project involved making composite films with the PPy in HSIII silicone. Each of PPy–EBSA, PPy–PSS and PPy–SO_4^{2-} were added to HSIII silicone to produce films with loading weights of 0, 1, 2, 4, and 8 % w/w. This enabled a comparison of the dielectric properties of PPy films having different dopants and films with different loading levels of the same dopant.

It was found that the real permittivity and loss factor increased as a function of filler loading for the three PPy+dopant systems. This is consistent with our findings from earlier work with ceramic fillers. Also, it appears that increased PPy oxidation (and hence conductivity) also leads to increases in the complex permittivity. Breakdown

strength is also affected, with the more conductive fillers leading to diminished breakdown strength. Ionic mobility however does not appear to influence significantly the breakdown strength.

Significance of Results

Although the literature has shown that conductive fillers can lead to permittivity increases as large as 10^4 [1], the increase in permittivity observed here was a more modest two-fold.

It is believed that conducting polymers will be advantageous for use as fillers in the dielectric elastomer layer of electroactive polymer (EAP) actuators because they should increase the permittivity of the elastomer without increasing the Young's modulus as much as the ceramic and inorganic fillers previously examined [2, 3].

It is believed that through the addition of conducting polymers, it is possible to increase the actuation stress of EAP actuators into a range where they will be practical for use on military platforms.

Future Work

This study was limited in its scope in that it examined a single filler/matrix combination, and that particle size and dispersion where not verified or varied in a controlled manner. Future work will include the examination of other conducting polymers such as polythiophene to better understand their effect on the elastomer. Different elastomer matrices may also be investigated. Polymers do not readily intermix, and finding a matrix polymer which interacts more favourably with the conducting polymer may change the electric and mechanical properties of the filler/matrix composite. These experiments are results oriented and aimed at identifying elastomeric composites suitable for use in Maxwell stress actuators.

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Sommaire

Contexte

Les matériaux actionneurs sont présents dans de nombreuses applications. Des exemples communs de ces matériaux sont les matériaux piézoélectriques, électrostrictifs, magnétostrctifs et à mémoire de forme. Les récents progrès dans le domaine des matériaux intelligents ont amené une nouvelle classe de dispositifs actionneurs utilisant des polymères électroactifs. Ces actionneurs se sont démontrés très prometteurs et se trouveront potentiellement utilisés pour l'isolation active du bruit pour des plate-formes militaires. Les polymères diélectriques utilisent l'effet de force Maxwell. La génération de cette force nécessite que la membrane élastomérique soit non-conductrice et qu'elle possède un petit module de même qu'une constante diélectrique élevée. On peut élever la constante diélectrique d'un élastomère en variant sa composition chimique ou en ajoutant des dopants comme des particules conductrices. Il a été démontré que la constante diélectrique peut être augmentée par un facteur de 104 pour des composites ayant aussi peu que 3% v/v charbon noir [1]. Notre but est d'imiter cette augmentation en utilisant un polymère conducteur comme charge. La recherche présentée ici discute de la synthèse du polymère polypyrrole et la formulation des films élastomeriques composites utilisant du polypyrrole dopé et du silicone à haute résistance. Les effets causés par le changement des ions de dopage et par la variation de la proportion polypyrrole verus silicone sur les propriétés diélectriques des composites seront discutés dans le document suivant.

Résultats Principaux

La recherche présentée ici a deux fronts distincts. Premièrement, du polypyrrole (PPy) a été synthétisé par une méthode préétablie par la littérature. Trois lots ont été créés, chacun incorporant un ion dopant différent. Les trois dopants étaient : acide sulfonique d'ethylbenzène (EBSA), sulfonate de polystyrene (PSS), et sulfate de sodium(SO_4^{2-}). Les produits PPy–EBSA, PPy–PSS,et PPy–SO_4^{2-} ont été analysés pour verifier la polymerisation et le point d'oxidation du PPy. On a trouvé que ce dernier est PPy–SO_4^{2-} <PPy–EBSA <PPy–PSS.

La deuxième partie du projet était de créer des films composites avec le PPy dans du silicone. Chacun des dopants, PPy–EBSA, PPy–PSS, et PPy–SO_4^{2-}, a été ajouté au silicone HSIII pour produire des films chargés à 0, 1, 2, 4, et 8% par poids. Ceci nous a permis de comparer les propriétés diélectriques des films de PPy ayant des différents dopants de même que des films avec un dopant où la charge varie.

Les résultats démontrent que la partie réelle de la permittivité de même que le fac-

teur de perte augmente en fonction du niveau de chargement du polymère conducteur. Ces résultats sont consistants avec les résultats obtenus lors de recherches étudiant les charges céramique. En plus, on observe qu'une augmentation du niveau d'oxydation (et donc la conductivité) entraîne aussi une hausse de la permittivité complexe. Une réduction de la résistance au claquage est par contre engendrée par l'augmentation de la charge conductrice. La mobilité ionique apparaît n'avoir aucun effet significatif sur la résistance au claquage.

Importance des Résultats

L'augmentation de la permittivité observée n'a été que d'un facteur de deux, même si la littérature rapporte qu'une augmentation d'un facteur de 10^4 [1] est possible.

L'utilisation de polymères conducteurs en tant que charge dans le noyeau élastomérique des actionneurs électroactifs est intéressant parce qu'ils devraient augmenter la permittivité sans augmenter le module de Young autant que les charges céramique et inorganique examinées au paravant [2, 3].

Par l'incorporation de polymères conducteurs, il devrait être possible d'augmenter la déformation des actionneurs électroactifs à un point tel qu'ils seront utiles pour des applications militaires.

Travaux Futurs

Cette étude était d'envergure limitée. Elle n'a examiné qu'une seule combinaison charge / matrice et il n'y a eu aucun contrôle de la grosseur ni la répartition des particules de dopant. Les travaux futurs incluront une étude de plusieurs autres polymères conducteurs tel que le polythiophène dans le but de mieux comprendre leurs effets sur l'élastomère. Il sera aussi possible d'investiguer l'utilisation d'élastomères différents. Car les polymères se mélangent difficilement, il est possible que l'utilisation d'une matrice qui interagit plus favorablement avec le polymère conducteur changera les propriétés électriques et mécanique du composite charge / matrice. Ces expériences sont orientées vers l'obtention de résultats et ont comme but d'identifier un composite élastomérique propice aux actionneurs à effet de Maxwell.

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1 Introduction

Dielectric polymer actuators exploit the Maxwell stress effect to induce motion in soft elastomers. These devices offer materials-based actuation having moderate stresses and large strains as well as good mechanical robustness. Consequently, they have been the object of much interest in recent years [4–7] for diverse applications such as loudspeakers, pump diaphragms, and artificial muscles.

When an electric field is applied to a pair of electrodes across a dielectric polymer membrane, the electrostatic attraction — Maxwell stress — between the electrodes compresses the polymer and causes an expansion of the polymer in the plane normal to this compression. For simple geometries and boundary conditions, the resulting stress σ and strain γ can be expressed [8] as a function of the polymer permittivity ε and Young's modulus Y and the applied electric field E:

$$\sigma = \nu\varepsilon\varepsilon_0 E^2 \tag{1}$$

$$\gamma = \frac{\nu\varepsilon\varepsilon_0 E^2}{Y} \tag{2}$$

where ε_0 is the permittivity of vacuum and ν is the Poisson's ratio of the film. $E = V/d$, where V is the applied voltage and d is the thickness of the dielectric core layer. The maximum performance is reached at E_b, the field at which the dielectric elastomer layer undergoes dielectric breakdown. Attempts have been made to model the contributions of electrical and material losses [9], electrode resistance [10], and DC bias [11] under small strains. Under large strains, hyperelastic material behaviour needs to be considered, as well as the changes in electrical field that occur as the film is stretched [12, 13].

It is evident from Equation 1 that the actuation response is directly proportional to the permittivity of the core layer and to the square of the applied electric field. One aspect of our research in this area has been the improvement of actuator performance using conductive [3, 14] and non-conductive [15] fillers. The present study introduces some preliminary work using conductive polymer fillers.

Electronically conductive polymers constitute a set of materials with unique properties. The conductivity of these polymers arises from the regular alternation of single and double bonds along the backbone, as seen in, for example, polypyrrole (Figure 1). This conjugation provides a quasi-infinite delocalized electronic band structure arising from the splitting of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) that exist in the parent monomer compound. The resulting valence band and conduction band, respectively, are reminiscent of the electronic structure of inorganic semiconductors.

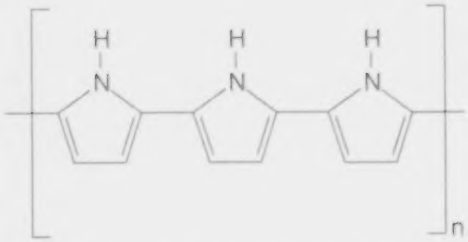

Figure 1: *Polypyrrole structure*

Like many inorganic semiconductors, most conducting polymers are natively insulating at room temperature and most be electrochemically modified (or "doped") to create charge carriers. In the case of polypyrrole, for example, the removal of an electron from the conduction band by oxidation (or p-doping) leaves a mobile positive charge that is free to move along the polymer backbone, Figure 2. It has been shown through electron spin resonance spectroscopy that individual charge carriers, or *polarons* of opposite spin join together, despite the electrostatic repulsion, to form spin-neutral *bipolarons* that span a few bonds. In order to maintain overall electroneutrality, the polarons or bipolaron must be balanced by counterions, often referred to as dopant ions (although these do not necessarily participate in the doping process itself). Hence, the electrical properties of the polymer can be ascribed to at least two factors: the number of charge carriers (*i.e.*, the degree of doping) and the nature of the counterion.

The purpose of this study was to conduct a preliminary investigation of the dielectric properties of conjugated polymer–silicone composites as potential candidates for Maxwell stress actuator core materials. Polypyrrole was chosen as the conjugated polymer, along with three counterions having very different mobilities: sulfate, ethylbenzene sulfonate, and poly(styrenesulfonate). These systems were examined to determine the influences of loading and counterion nature upon complex permittivity and dielectric breakdown strength.

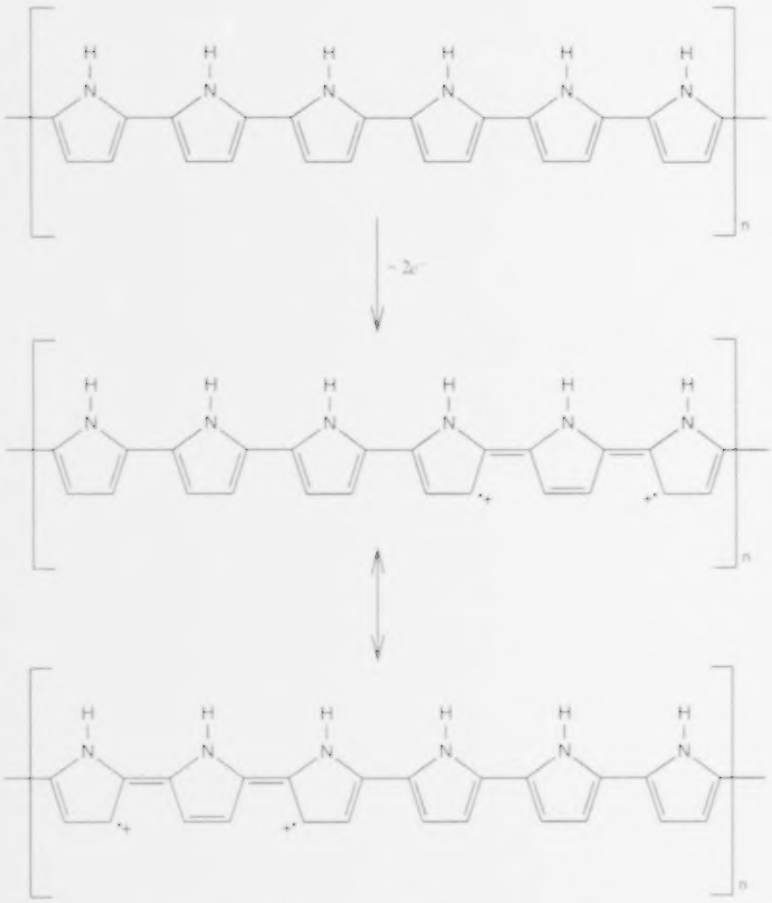

Figure 2: *Example of the oxidation of polypyrrole generating mobile bipolaron charge carriers*

2 Experimental

All reagents were purchased from Sigma-Aldrich and used as received unless otherwise stated.

2.1 Synthesis of polypyrrole

Polypyrrole (PPy) was synthesized in accordance with widely used literature methods [16,17]. Pyrrole was purified by passing the liquid through an alumina column, and 0.96 g (14 mmol) added slowly to a solution containing 2 mole equivalents of one of the three dopant counterions: sodium sulfate (SO_4^{2-}), ethylbenzene sulfonic acid (EBSA), and sodium polystyrene sulfate (PSS) in 50 mL deionized water. Two mole equivalents of ammonium persulfate solution (1.75 mol/L) were then added. A fine black solid formed immediately, and the resulting mixture was stirred 24 hours under an inert atmosphere.

The doped PPy was isolated by centrifugation followed by filtration through a 0.45 μm filter and washing with deionized water. The resulting solid was dried *in vacuo* for 15 h at 60 °C. It was subsequently ground and passed through a 67 μm sieve to achieve a uniform particle size.

2.2 Polypyrrole characterization

2.2.1 Elemental analysis

Elemental analyses (carbon, hydrogen, nitrogen, and sulfur) were performed by Canadian Microanalytical Services, Delta, BC.

2.2.2 Infrared spectroscopy

Determination of pyrrole polymerization was carried out by Fourier transform infrared spectroscopy. The polypyrrole sample was ground with sodium chloride to form a fine powder. The powder was then packed into a diffuse reflectance sample holder. The absorbance spectrum was obtained between 700 cm^{-1} and 4000 cm^{-1} and compared with the literature [18].

2.3 Preparation of composite films

HSIII RTV High Strength Silicone Rubber (Dow Corning Corp., Midland MI) was filled with doped PPy. Three batches of PPy were synthesized, each doped with

one of three different dopants: ethylbenzenesulfonic acid (EBSA), poly(styrene-4-sulfate) (PSS) and sodium sulfate (SO_4^{2-}). Each batch of doped PPy was mixed with the silicone to yield composite films having loadings of 0%, 1%, 2%, 4% and 8% (w/w) PPy+dopant respectively. Mixing of the PPy+dopant/silicone composites was accomplished using a double planetary mixer (Charles Ross & Son Company, Hauppage, NY). The mixing was performed under vacuum with an orbital speed of 20 rpm. The HSIII consisted of two parts, a silicone pre-polymer base and a curing agent (cross-linker). To ensure adequate dispersion of the PPy+dopant in the silicone, those two components were premixed for five minutes. The cross-linker was then added, and the whole blend was mixed for a further ten minutes.

The viscous blend was then spread on a glass plate that was previously treated with a releasing agent (Ivory® dish soap). Uniform film thickness was achieved using standard wet-film applicators (Gardco, Pompano Beach, FL). The wet film thicknesses were 375, 750 and 2500 μm. The films were allowed to cure at room temperature until they were no longer tacky to the touch (1 to 5 days). A canopy was erected over the samples while they cured to reduce contamination from airborne particulate. Once curing was complete, the films were released from the glass using tap water. The films were rinsed with additional tap water to remove any residual releasing agent.

2.4 Characterization of composite films

2.4.1 Dielectric permittivity

Permittivity measurements were determined using a Dielectric Analyser 2970 (DuPont Instruments) with Thermal Analysis software. Samples (25 mm × 25 mm) were cut from a 750 μm thickness film and analysed. Each sample involved a temperature equilibration at 20 °C, followed by a frequency sweep (0.1 Hz–200 kHz). The resulting permittivity and loss factor data was reported as a function of frequency.

2.4.2 Dielectric breakdown

Prior to measuring dielectric breakdown, the film thickness was measured using a thickness gauge (Gardco, Pompano Beach, FL) which utilized eddy current principles. As can be seen from Equation 2, the strain is directly proportional to the electric field strength. Thus maximum performance occurs when the highest electric field is reached before the dielectric elastomer fails. As such, it is important that the electric field at which the elastomer breaks down be determined. It turns out that such breakdown is often precipitated by defects in the film, and not the intrinsic properties of the material. To minimize the influence of these manufacturing

effects, a point contact approach was developed thus reducing the likelihood of a physical defect being present in the region in question.

The apparatus is illustrated schematically in Figure 3. The sample films were placed on an aluminium plate, which served as an electrical contact. The second electrical contact was made using the edge of a ring terminal through a small opening in an insulating layer. The voltage was ramped at approximately 100 V/s until breakdown occurred, and the corresponding voltage was observed at the amplifier monitor output using a Fluke 189 multimeter.

3 Results and Discussion

3.1 Characterization of polypyrrole

3.1.1 Elemental analysis

Elemental analyses for the three PPy+dopant systems are presented in Table 1. Calculated element proportions assume a degree of oxidation corresponding to 0.25 dopant ions per pyrrole unit. The atom ratio of sulfur to nitrogen is a convenient measure of this ratio. The PPy–EBSA sample was found to have a dopant content consistent with the predicted degree of oxidation. PPy–SO_4^{2-} exhibited a significantly lower dopant ion content (although this could also be in part reflective of the divalent nature of this counterion), indicating a system with reduced charge carrier density and consequently diminished conductivity. The dopant ion content of PPy–PSS was much higher than predicted, indicating increased conductivity, although in this case it is difficult to separate the contribution of counterions present for charge balance and those locked in the blend as a result of the polymeric nature of this dopant.

	Calc					Found				
	C	H	N	S	S:N	C	H	N	S	S:N
PPy–SO_4^{2-}	53.9	3.4	15.7	9.0	0.25	44.06	3.29	12.94	2.22	0.08
PPy–EBSA	64.7	4.7	12.6	7.2	0.25	47.15	4.07	11.96	7.77	0.28
PPy–PSS	64.7	4.7	12.6	7.2	0.25	22.81	3.95	6.50	19.44	1.31

Table 1: *Carbon, hydrogen, nitrogen and sulfur elemental analyses of the polypyrrole samples prepared using sulfate, ethylbenzene sulfonic acid, and polystyrene sulfonate as dopants.*

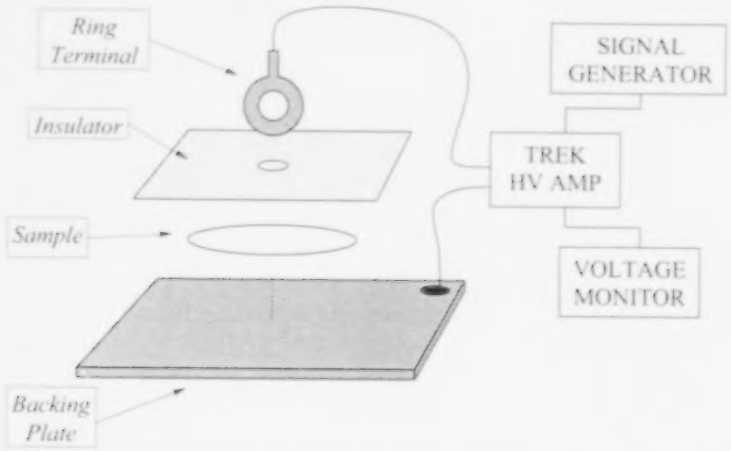

Figure 3: *Schematic of the point contact dielectric breakdown apparatus*

3.1.2 Infrared spectroscopy

Polypyrrole consists of five-membered rings linked together to form a conjugated chain (Figure 1). It is known that the baseline measured when analysing conducting materials has a tendancy to slope due to a plasma reflection phenomena [19]. The unique characteristics include nitrogen-hydrogen bonds which can participate in hydrogen bonding, and both C–N and C–H ring stretching. The literature lists a band at 1549 cm^{-1}, due to stretching of the five-membered ring through the C–N bond, a band at 1485 cm^{-1}, due to the conjugated C–N bond stretching, a broad band at 3403 cm^{-1}, due to N–H hydrogen bonding and small peaks at 2925 and 2851 cm^{-1}, due to five-membered ring C–H ring stretching. The spectrum for PPy–SO_4^{2-} shows the bands at 3400 and 1549 cm^{-1} but the slope in the baseline is too extreme to determine any of the other significant PPy bands. The spectrum for PPy–EBSA shows the bands at 3400 and 1549 cm^{-1}. Peaks appear at approx. 2900 cm^{-1} that can be attributed to either the C–H wagging in PPy or to sulfonate groups. It also shows sulfonate peaks at approx. 1185 cm^{-1}, which are typical for para-toluene sulfonates. The baseline for the PPy–PSS spectrum sloped considerably and made it difficult to make determinations of the bands. There is a substantial band at > 3300 cm^{-1} which may be attributable to N–H hydrogen bonding. Another slight band appears at approx. 1549 cm^{-1} which may be the C–N ring stretching. A large peak is observed at 1185 cm^{-1}, typical of para-toluene sulfonates. Although the slope to the baseline makes it impossible to have a definitive identification of the polypyrrole samples, there are a number of peaks in common with literature spectra to suggest that all three samples have polymerized to form PPy. The IR data in addition to the insolubility of the sample and the elemental analysis data (see

§3.1.1) provide evidence that the pyrrole was polymerized.

3.2 Electrical Properties of Composites

3.2.1 Dielectric permittivity

Figures 4, 5, and 6 summarize the complex permittivity responses of silicone composites of the three PPy+dopant fillers at various loading levels. The real permittivity ε' and loss factor ε'' increase as a function of filler loading level. This trend is consistent with results from earlier work with ceramic fillers [2].

Figure 7 summarizes the complex permittivity for all composites at 10 Hz, an arbitrary frequency. Loading levels in this figure are for PPy only; mass was corrected by removing the contribution of counterion content as indicated by elemental analysis data (see §3.1.1). In Section 3.1.1 it was shown that the inferred degree of PPy oxidation (and consequently conductivity) increases in the order PPy–SO_4^{2-} < PPy–EBSA < PPy–PSS. This trend is reflected in Figure 7A, demonstrating that the permittivity is a function of both the loading level and the implied conductivity of the filler material. The filler materials were not synthesized in sufficient quantities to measure their explicit dry conductivities.

3.2.2 Dielectric breakdown

Based on Equations 1 and 2, the performance of an actuator is proportional to the square of the electric field strength, V/d. Dielectric breakdown occurs when a threshold field is exceeded, resulting in destructive arcing through the film. Hence, to obtain optimum performance, the actuator must be run at the highest possible electric field below the dielectric breakdown threshold E_b.

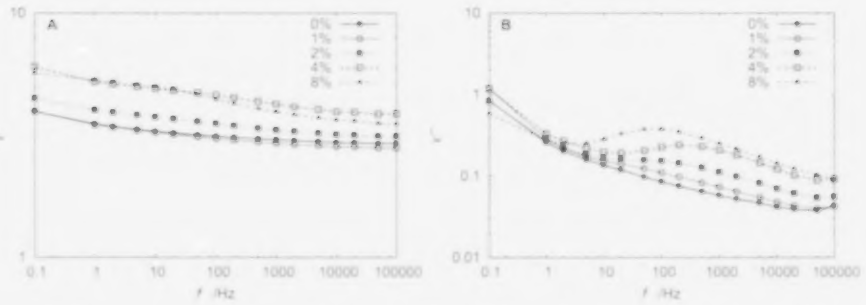

Figure 4: Dielectric permittivity (A) and loss factor (B) in composites of HS-III and polypyrrole containing sulphate ions.

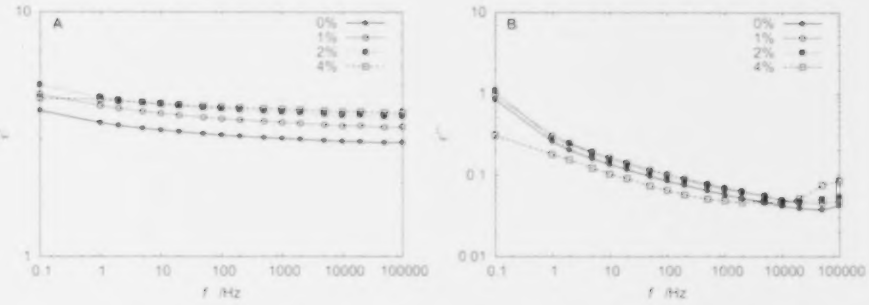

Figure 5: *Dielectric permittivity (A) and loss factor (B) in composites of HS-III and polypyrrole containing ethylbenzene sulphonate ions.*

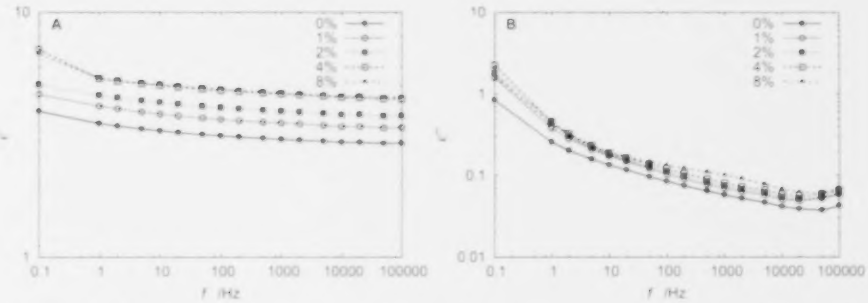

Figure 6: *Dielectric permittivity (A) and loss factor (B) in composites of HS-III and polypyrrole containing polystyrene sulphonate ions.*

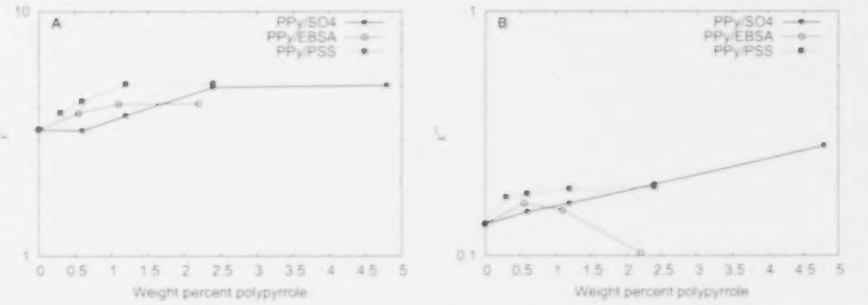

Figure 7: *Dielectric permittivity (A) and loss factor (B) trends at 10Hz. Polypyrrole loading is derived from elemental analysis data.*

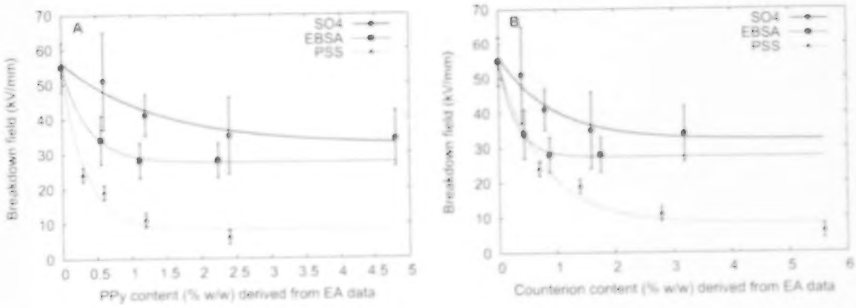

Figure 8: *Dielectric breakdown as a function of (A) doped pyrrole content and (B) counterion content in filled HS-III composites. Data was fit to an exponential decay.*

Figure 8A shows that as filler content increases, the dielectric breakdown strength decreases. This trend is consistent with our previous work with ceramic fillers [2]. Furthermore, dielectric breakdown strength decreases in the order PPy–PSS < PPy–EBSA < PPy–SO_4^{2-}. This follows the degree of oxidation of the conducting polymer as established in Section 3.1.1. A possible contributor to breakdown is the presence of mobile ionic species in the composite. In Figure 8 the breakdown strength is plotted as a function of counterion content. Ionic mobility increases[1] in the order EBSA < SO_4^{2-} < PSS. While PSS, the most ionically conductive species, does indeed produce the composite with lowest breakdown strength. However, the order of EBSA and sulfate are reversed. In this case, it can be concluded that counterion mobility is not a factor governing the breakdown strength of the composite.

Therefore it is clear that at least two phenomena contribute to dielectric breakdown in conducting polymer-filled composites: filler loading level and filler conductivity.

4 Conclusions

A comparison of different dopants for PPy and different PPy+dopant loadings in HSIII silicone was performed. Polypyrrole was synthesized using a literature method and sodium sulfate, ethylbenzene sulfonic acid, and sodium polystyrene sulfonate were used as three dopant counterions. The conductivity of the PPy+dopant was found to increase as PPy–SO_4^{2-} < PPy–EBSA < PPy–PSS, which may explain the dielectric breakdown of PPy+dopant/HSIII films. Increasing the weight percent of

[1]The diminished mobility of EBSA compared to sulfate is easily explained by the bulkiness of the former. The sulfate groups in PSS are however immobilized in a polymer matrix. The increased ionic conductivity of PSS is explained by the presence of protons which may migrate through the polymer matrix, hopping between nearby pendent sulfonate groups. This behaviour is exploited in materials such as DuPont's Nafion, frequently used as a proton exchange membrane in fuel cells.

PPy+dopant in the HSIII matrix corresponded to an These results can be applied in a practical sense to high dielectric polymers for actuator and energy storage applications. The findings are preliminary, and a more rigorous study ought to encompass aspects such as better characterization of the filler materials and enhancement of the filler–matrix interaction through a more judicious selection of host polymer.

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4. AUTHORS (Last name, first name, middle initial. If military, show rank, e.g. Doe, Maj. John E.)

Cameron, Colin G. ; Murphy, Jason P. ; Underhill, Royale S.

5. DATE OF PUBLICATION (month and year of publication of document)

July 2004

6a. NO. OF PAGES (total containing information. Include Annexes, Appendices, etc).

27

6b. NO. OF REFS (total cited in document)

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Dielectric polymer actuators that utilize the Maxwell stress effect consist of a thin membrane of elastomer sandwiched between compliant electrodes. When an electrostatic charge is applied across the electrodes, the oppositely charged electrodes attract, resulting in an expansion of the polymer in the plane normal to the compression. In order to maximize performance, the dielectric layer must be non-conducting and have a low Young's modulus and a high dielectric constant. Increasing the dielectric constant of an elastomer can be achieved by adding conductive fillers below the percolation threshold. The goal of this research was to increase the dielectric constant of a silicone elastomer through the addition of a conducting polymer filler. Three different sulfate doped polypyrroles (PPy) were synthesized using a literature method. Composite films using the PPy+dopant filler and a high strength silicone were formed and used to study the effects of changing the dopant and the PPy:silicone ratio on the dielectric properties of the composite film. The different dopant counterions used were sulfate (SO_4^{2-}), ethylbenzene sulfonic acid (EBSA) and polystyrene sulfonate (PSS). The conductivity of the PPy+dopant was found to increase as PPy–SO_4^{2-} < PPy–EBSA < PPy–PSS. Increasing the weight percent of PPy+dopant in the silicone matrix corresponded to an increase in the permittivity. These results supply valuable information for the use of high dielectric polymers in actuator and energy storage applications.

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